

General Disclaimer

One or more of the Following Statements may affect this Document

- This document has been reproduced from the best copy furnished by the organizational source. It is being released in the interest of making available as much information as possible.
- This document may contain data, which exceeds the sheet parameters. It was furnished in this condition by the organizational source and is the best copy available.
- This document may contain tone-on-tone or color graphs, charts and/or pictures, which have been reproduced in black and white.
- This document is paginated as submitted by the original source.
- Portions of this document are not fully legible due to the historical nature of some of the material. However, it is the best reproduction available from the original submission.

STUDY OF REMOVAL OF AMMONIA FROM URINE VAPOR BY DUAL CATALYST

Final Report

by
P. Budininkas

November, 1976

Prepared Under Contract No. NAS2-9219

by

GATX

GARD, INC.

7449 NORTH NATCHEZ AVENUE
NILES, ILLINOIS 60648

for

**AMES RESEARCH CENTER
NATIONAL AERONAUTICS AND SPACE ADMINISTRATION**

N77-14732

Unclass
58990

G3/51

CSCL 06B

(NASA-CR-151930) STUDY OF REMOVAL OF
AMMONIA FROM URINE VAPOR BY DUAL CATALYST
Final Report, May - Oct. 1976 (GARD, Inc.,
Niles, Ill.) 40 P HC A03/MF A01



STUDY OF REMOVAL OF AMMONIA FROM URINE VAPOR
BY DUAL CATALYST

Final Report

by

P. Budininkas

November, 1976

Distribution of this report is provided in the interest of
information exchange. Responsibility for the contents
resides in the author or organization that prepared it.

Prepared Under Contract No. NAS2-9219

by

GATX/GARD, INC

Niles, Illinois 60648

for

AMES RESEARCH CENTER
NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

FOREWORD

The development work described herein was conducted by GARD, INC/GATX during the period of May, 1976 through October, 1976 under NASA Contract NAS2-9219. The Project Engineer was P. Budininkas. The contract's Technical Monitor was P. D. Quattrone, Chief, Environmental Control Research Branch, NASA Ames Research Center, Moffett Field, California.

TABLE OF CONTENTS

	Page
LIST OF FIGURES	iv
LIST OF TABLES	v
SUMMARY	1
INTRODUCTION	2
SURVEY OF LITERATURE	5
SCREENING OF CATALYSTS	10
Experimental Apparatus and Procedures	10
Oxidation of Ammonia	13
Catalytic Decomposition of Nitrous Oxide	15
Dual-Catalyst Tests	21
REMOVAL OF AMMONIA FROM URINE VAPOR	26
CONCLUSIONS AND RECOMMENDATIONS	32
BIBLIOGRAPHY	34

LIST OF FIGURES

<u>Figure</u>		<u>Page</u>
1	System for Screening of Catalysts	11
2	Dual-Catalyst System for Treating Urine Vapor	27

LIST OF TABLES

<u>Table</u>		<u>Page</u>
1	Low Temperature Catalytic Oxidation of Ammonia	16
2	Catalytic Decomposition of Nitrous Oxide	22
3	Ammonia Removal by Dual Catalyst Arrangement	24
4	Removal of Ammonia from Urine Vapor	29
5	Typical Quality of Recovered Water	30

SUMMARY

The feasibility of ammonia removal from urine vapor by a low temperature dual-catalyst system was investigated. The process is based on the initial catalytic oxidation of ammonia (NH_3) present in urine vapor to nitrogen (N_2) and nitrous oxide (N_2O), followed by a catalytic decomposition of the N_2O formed into its elements.

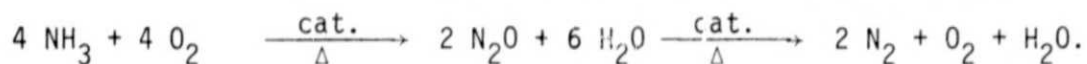
Potential ammonia oxidation catalysts, selected on the basis of a literature study, were first screened with artificial gas mixtures containing constant concentrations of ammonia. Another series of screening tests was performed with potential N_2O decomposition catalysts, also using artificial gas mixtures. The most active catalysts for the oxidation of ammonia and for the decomposition of N_2O , identified in screening tests, were then combined into dual-catalyst systems and tested to establish their overall efficiencies for the removal of ammonia from artificial gas mixtures.

Dual-catalyst systems capable of ammonia removal from the artificial gas mixtures were then tested with the actual urine vapor produced by boiling untreated urine. A suitable dual-catalyst bed arrangement was found that achieved the removal of ammonia and organic carbon, and recovered water of good quality from urine vapor.

INTRODUCTION

In the recovery of water from urine, a major problem common to present urine treatment systems is their inability to deal satisfactorily with the ammonia present in urine and/or urine vapors. Although free ammonia is present in urine in relatively small quantities, urea slowly hydrolyzes forming ammonia and carbon dioxide. Since ammonia is a stable and volatile molecule that has very strong affinity for water, it is readily transferred unchanged from urine to the recovered water. Therefore, most of the urine treatment techniques employ either pretreatments or additives for minimizing the formation of ammonia, or post-treatment steps for removing the ammonia carried to the recovered water, or both. These measures, of course, add to the complexity, weight, and volume of the water recovery system and to the expendables.

The objective of this investigation was to demonstrate the feasibility of ammonia removal from urine vapor by conversion to innocuous gas and water vapor in a low-temperature dual-catalyst system. The catalytic process is based on the initial catalytic oxidation of ammonia to nitrous oxide (N_2O) that is then decomposed catalytically into its elements, according to the following overall reaction:



The product of the catalytic oxidation of ammonia may contain a mixture of N_2 , N_2O , and NO ; however, one reaction product may predominate, even up to a nearly complete exclusion of others, depending on the re-

action conditions, temperature, and the catalyst used. For the purpose of ammonia removal from urine, oxidation of ammonia to nitrogen would be ideal. Unfortunately, this reaction never proceeds alone at practical rates and is always accompanied by reactions producing either N_2O or NO , or both. The main problem, therefore, is to discover ammonia oxidation catalysts and experimental conditions that would produce a mixture of N_2 and essentially harmless N_2O , without forming any NO that, in the presence of oxygen, spontaneously converts into a toxic mixture of NO and NO_2 , generally designated as NO_x . The N_2O formed can be then catalytically decomposed into its elements.

The dual-catalyst treatment of urine vapor not only achieves the conversion of NH_3 into N_2 but also oxidizes volatile organics to CO_2 and effects a sterilization of the vapor. Thus, water can be recovered from urine in an evaporative, relatively low-temperature and ambient pressure operation requiring no additives for urine stabilization or post-treatment steps. The decomposition of urea into NH_3 and CO_2 during the evaporation of urine, followed by the conversion of NH_3 into N_2 and H_2O actually results in a reduction of volume and weight of the remaining sludge.

The following approach was employed for achieving the objective of this investigation:

1. A literature survey and study was performed to identify available catalysts and catalytic materials suitable for the low-temperature oxidation of ammonia into N_2 and N_2O and low-temperature decomposition

of N_2O into its elements.

2. Selected catalysts were screened in the laboratory using single-pass reactors for their effectiveness for

- a. oxidation of NH_3 to N_2 and N_2O
- b. decomposition of N_2O into its elements

The screening of catalysts was performed with artificial, constant concentration mixtures containing either NH_3 or N_2O .

3. The most effective catalysts for the oxidation of NH_3 and for the decomposition of N_2O were combined in dual-catalyst arrangements and were tested with an artificial mixture containing fixed concentration of NH_3 to establish their overall capabilities for the removal of NH_3 .

4. Dual-catalyst bed combinations found to be the most effective for the removal of NH_3 from artificial gas mixtures were evaluated with actual urine. The vapor of untreated urine was mixed with air and passed through the dual-catalyst arrangement; then water was recovered by condensation and analyzed to establish its quality.

SURVEY OF LITERATURE

Literature Search.- A literature search pertaining to the low temperature oxidation of ammonia and to the catalytic decomposition of nitrous oxide was performed, starting with recent publications and extending back through 1949. It was felt that publications earlier than 1949 were adequately covered by review articles and books. Both computerized and manual search methods were employed. Since chemical abstracts are computerized only from approximately 1970 to date, search of literature abstracted prior to 1970 was performed manually.

The basic source of the literature search was Chemical Abstracts; however, other abstracting publications such as Air Pollution Abstracts, Government Report Index, and published review articles and books were also used. The general subject headings used in all phases of the literature search were:

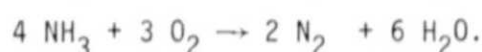
1. Low temperature catalytic oxidation of ammonia (NH_3) to nitrogen (N_2) and nitrous oxide (N_2O), including the following sub-headings: oxidation to N_2 , oxidation to N_2O , catalysts, reaction mechanism, kinetics, thermodynamics. Excluded from the search were oxidation of ammonia to nitric oxide (NO) or to nitrogen dioxide (NO_2), and oxidation at temperatures exceeding 500°C .

2. Catalytic decomposition of nitrous oxide (N_2O), including sub-headings: catalysts, reaction mechanism, kinetics, thermodynamics.

The abstracts of all the articles identified by the search were obtained, classified, and carefully reviewed for pertinency. Copies

of the pertinent publications were then obtained for detailed study. The basic, and most pertinent publications on the study subjects are listed in the Bibliography.

Catalytic Oxidation of Ammonia.- The oxidation of ammonia on solid catalysts can proceed along three basic reaction paths, namely:



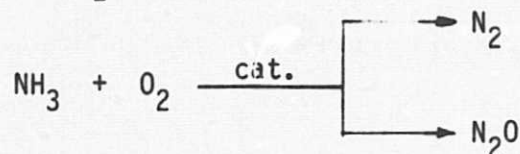
In the presence of suitable catalysts, the reaction product may contain a mixture of NO, N₂O, and N₂; however, the relative concentrations of these products depends on reaction conditions, temperature, and the catalyst employed, and one reaction product may predominate even up to a nearly complete exclusion of others. Thus, in selecting ammonia oxidation catalysts and experimental conditions for obtaining a desired product, both the catalytic activity and the selectivity must be considered.

At high temperatures, the predominant product of ammonia oxidation is NO. Low temperature oxidation favors the formation of N₂ and N₂O, with practically no NO formed at temperatures below 250-300°C.

Recently, in a series of publications, Il'chenko and Golodets (1, 2, 3, 4, 5, 6)* have considered the low temperature oxidation of ammonia using their own and previously published data. On the basis of experimental data with various oxidation catalysts at temperatures ranging from 100°C to 370°C, they established that the oxidation of

*Numbers in parenthesis indicate publications listed in the Bibliography.

ammonia to N_2 and to N_2O proceed by two independent, parallel paths:



At 300°C, the activity of metallic catalysts for the overall oxidation of ammonia can be expressed in the following approximate order: $Pt > Pd > Cu > Ag > Ni > Au > Fe > W > Ti$. The activity of metal oxides follows essentially the same order. However, the selectivity toward the formation of N_2 is the reverse of the order expressing the overall oxidation activity. It is interesting that the initial formation of N_2 was always observed at temperatures lower than those required for the initial formation of N_2O . Thus, the least active catalysts at low temperatures may form essentially N_2 but the rate of conversion is impractically low.

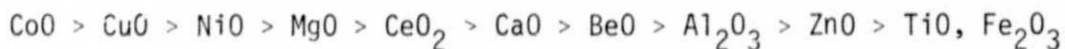
Essentially all the published data were obtained with mixtures of ammonia and oxygen, and using high ammonia concentrations; for instance, Il'chenko and Golodets data were obtained mostly with partial pressures of NH_3 in the 0.1 atm range and partial pressures of O_2 up to 0.9 atm. To obtain kinetic data, experiments were generally performed under conditions producing low conversion of ammonia (up to 20%). With a given catalyst, the selectivity to either N_2 or N_2O is influenced by the experimental conditions, namely the temperature and the ratio of oxygen to ammonia in feed gas. Lowering the temperature results in an increase in the N_2 formation; however, at the loss of overall ammonia oxidation. An increase in the O_2/NH_3 ratio results in an increase in

the formation of N_2O . However, the contact time does not show any influence either to the overall oxidation rate or to the selectivity of N_2 or N_2O formation.

Although the conditions encountered in the removal of ammonia from urine vapor are entirely different (i.e., low NH_3 concentrations, relatively high O_2/NH_3 ratio, presence of other gases and vapors) and an essentially complete removal of NH_3 is desired, the above observations form a basis for the selection of catalysts and experimental conditions, and provide indication of results obtainable.

Catalytic Decomposition of N_2O .— The decomposition of nitrous oxide into its elements on catalytic surfaces has been investigated in many studies concerned with the theory of catalysis, particularly in attempts to relate catalytic activity with the electronic state of the catalyst. Since the main concern was the elucidation of the catalyst behavior, usually no effort was made to achieve a complete decomposition of the N_2O .

Most of the data concerning the catalytic decomposition of N_2O were obtained using either pure N_2O , or N_2O and N_2 mixtures, but in the absence of O_2 . The decomposition is initially first order with respect to N_2O ; however, it becomes retarded as the reaction proceeds due to poisoning of catalyst surface by the oxygen formed during the decomposition. With feed gas containing no oxygen, the approximate order of catalytic activity of metal oxide catalysts was found to be (28).



and the temperature required to achieve a 50% decomposition ranged from 265°C to 730°C. On the basis of the temperature required to produce measurable decomposition of N_2O , metal oxide catalysts can be divided into three groups (27):

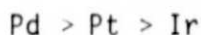
1. Active below 400°C, consisting of Cu_2O , CoO , Mn_2O_3 , NiO , CuO
2. Active in the 400°-500°C range, such as CaO , MgO
3. Active above 550°C, such as Al_2O_3 , CdO , TiO_2 , Cr_2O_3 , Fe_2O_3 .

The decomposition of N_2O present in low concentration (10-1000 ppm) in oxygen has been studied in the temperature range of 230°-550°C (26). Similarly to gas feed containing no O_2 , the kinetics were first order with respect to N_2O . The order of catalytic activity was found to be



and up to 85% decomposition of N_2O was observed.

Platinum Group metals are active for the decomposition of N_2O ; however, the influence of oxygen is in dispute (24,25). The general order of catalytic activity is reported as



and oxygen, either present in feed or produced during the decomposition, is considered a surface poison. However, the catalytic efficiency of PdO has been reported greater than that of the metal (25), provided the oxygen concentration exceeds the dissociation pressure of PdO .

SCREENING OF CATALYSTS

Selected catalysts were screened in two separate series of tests to determine their effectiveness for

- a. Oxidation of NH_3 to N_2 and N_2O
- b. Decomposition of N_2O into its elements

To achieve a meaningful comparison of their activities, catalysts of each series were tested under identical conditions. Since the composition of actual urine vapor does not remain constant on continuous evaporation, screening of catalysts was performed with artificial gas mixtures containing either NH_3 or N_2O in concentrations anticipated for urine vapor.

Experimental Apparatus and Procedures

Screening of catalysts, both for the oxidation of NH_3 and for the decomposition of N_2O , was performed in an arrangement shown schematically in Figure 1. The reactor was a 30mm O.D. Pyrex glass tube surrounded by a 20 cm (8") long electric heater for maintaining a desirable temperature. A thermocouple well located in the longitudinal center of the reactor contained thermocouples used for the control and measurement of the catalyst bed temperature.

The catalyst was located in the center of the heated zone supported on Pyrex glass wool. The volume of the catalyst used was 50 cc; thus, the length of the catalyst bed was approximately 10 cm (4"). Because

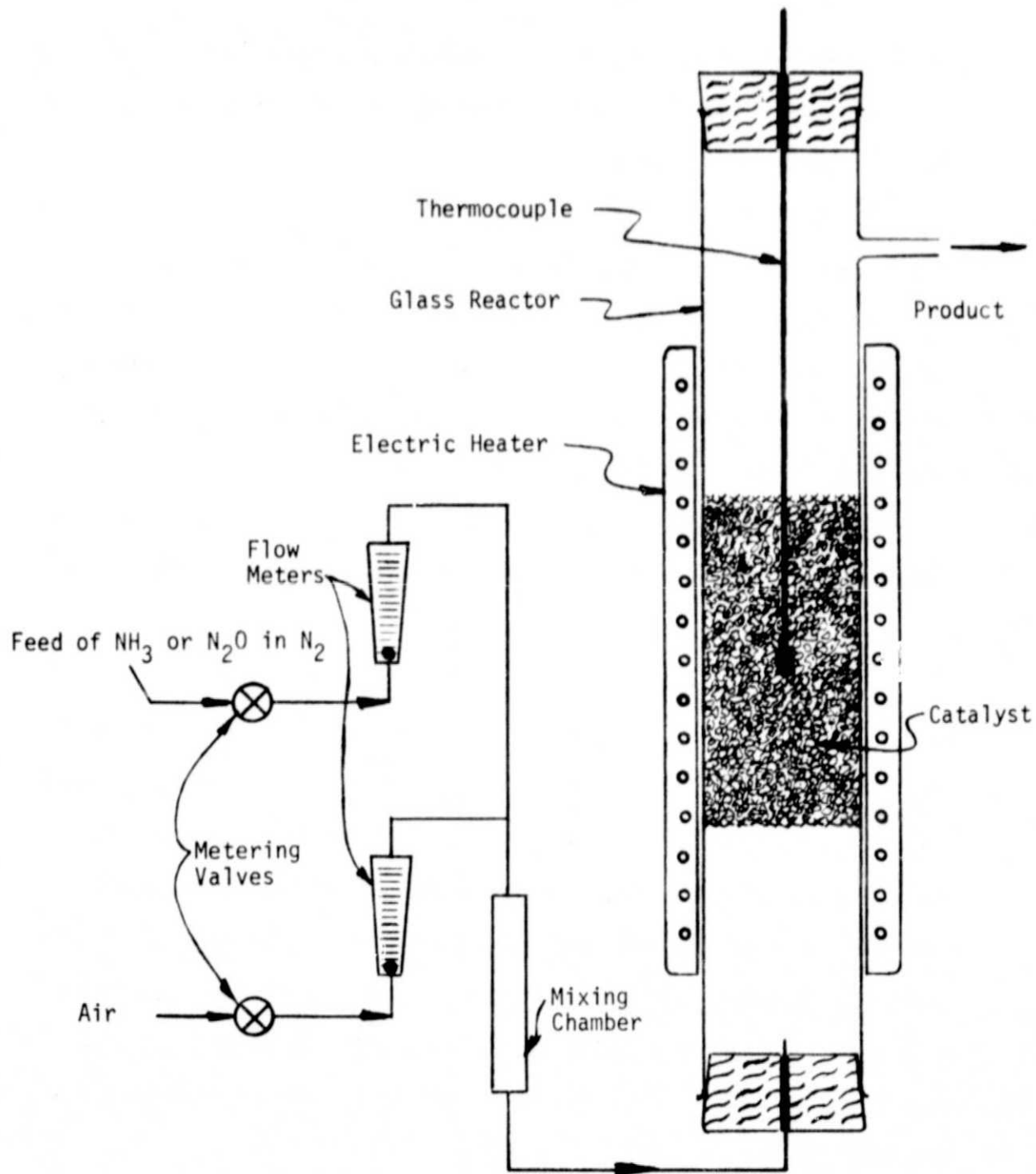


Figure 1. SYSTEM FOR SCREENING OF CATALYSTS

the electric heater extended 5 cm (2") below and above the catalyst bed, end effects were minimized and a relatively uniform temperature through the catalyst bed was obtained.

The feed gas was passed through the catalyst bed at a uniform rate of 1000 cc/min, i.e., a space velocity of 1200 hr^{-1} . Feed gas of desired concentration was prepared by dynamic blending of measured streams of gas mixtures containing known concentrations of either NH_3 or N_2O in nitrogen with purified air in proportions required for obtaining the desired concentration of NH_3 or N_2O .

The extent of reaction was followed by appropriate analyzes of the feed and of the product gas. The following analytical techniques were used:

- a. A spectrophotometric method for ammonia using alkaline phenol, and sodium hypochlorite reagent (B. W. Grunbaum and N. Pace, Microchemical Journal, 9, 166, 1965) was used both for feed and for product gases. This method is sufficiently sensitive to detect ammonia in gas at less than 1 ppm and, by varying the sample size, can also be used for the feed gas containing 1000 ppm. Ammonia present in the gas stream is captured in slightly acidified water. After the development of color by reagents, ammonium ion concentration is determined from absorbance at 630 nm (630 $\text{m}\mu$) wavelength and is then related to the NH_3 concentration in the gas.
- b. A gas chromatographic method using a thermal conductivity detector and a Porapak N column was found adequate for N_2O . The detection

limit is 5 ppm when a 5.0 cc sample of untreated gas is used. However, the sensitivity can be increased to 1 ppm (or even to ppb range) by a concentration method where N_2O from a large gas sample is first adsorbed on a short adsorbent column, then released by heating and flushed with helium into the gas chromatograph.

c. A modified Saltzman method was used for determining the NO_x (i.e., $NO + NO_2$) in product gas. Color is developed by reacting NO_2 with a reagent consisting of a mixture of sulfanilic acid, N- (1-naphthyl) ethylenediamine dihydrochloride, and acetic acid, and the concentration is read from the absorbancy at 550 nm (550 m μ) wavelength. Since this method measures only the concentration of NO_2 , NO present in product gas must first be converted into NO_2 . This is accomplished readily by mixing a sample of product gas with equal volume of oxygen. By employing adequate sample volumes, 1 ppm of combined NO and NO_2 in gas can be detected. Nitrous oxide (N_2O) does not interfere and is not detected by this method.

Oxidation of Ammonia

The activities of selected ammonia oxidation catalysts were tested under identical conditions. Tests were performed using catalyst bed of 50 cc, feed gas space velocity of 1200 hr⁻¹, and temperatures of 200°, 250°, and 300°C (392°, 482°, and 572°F). Nitrogen containing a known concentration of NH_3 was mixed dynamically with air in proportions required for obtaining a nominal 1000 ppm by volume concentration of NH_3 .

in the feed. This concentration of NH_3 was selected on the basis of past experience with evaporative treatment of fresh sewage from a low volume flush commode indicating that the ammonia concentration of the vapor is in the 500-1000 ppm range.

Before testing, each catalyst was heated to and maintained at approximately 325-350°C (617°-662°F) with the air flowing through it until the effluent was free of NO_x . This pretreatment was found necessary because most of the catalysts were prepared from metal nitrates and contained residual nitrate that produces NO_x on heating, causing erroneous NO_x readings in the product gas.

Testing of each catalyst was initiated by first adjusting the feed gas flow and NH_3 concentration, then slowly heating the catalyst bed to the lowest test temperature (i.e., 200°C) and maintaining these conditions until the ammonia concentration in the product gas becomes constant. Initially, ammonia is removed from the gas stream by adsorption on the fresh catalyst. Only when an equilibrium is established and the NH_3 concentration in the product remains constant, the measured removal of ammonia can be attributed to its oxidation into N_2 and N_2O . Similarly, tests at 250°C and 300°C were performed by slowly raising the catalyst bed temperature and observing that adsorption equilibrium is established before analyzing the product gas for ammonia oxidation products.

Product gas was analyzed for NH_3 , N_2O , and NO_x ; at least two samples were analyzed at each temperature. To facilitate screening of catalysts,

simplified analytical procedures were employed resulting in the detection limits of 5 ppm for NH_3 , 7.5 ppm for N_2O , and 5 ppm for NO_x . For this reason, whenever NH_3 , N_2O or NO_x was not found in the product, it was reported as not detectable instead of not present.

The results of tests with the ammonia oxidation catalysts are summarized in Table 1. The experimental results indicate that the catalysts can be grouped into three groups, namely:

1. Low activity catalysts, producing a partial removal of ammonia.
2. Active catalysts, removing NH_3 completely by oxidation into a mixture of N_2 and N_2O .
3. Strong oxidation catalysts, removing NH_3 completely but producing unacceptable concentrations of NO_x as one of the products.

Since the direct oxidation of NH_3 into N_2 is of obvious interest, catalysts of group 1 that showed high selectivities of N_2 formation were investigated further by doubling the contact time, i.e., decreasing the space velocity to 600 hr^{-1} . However, the increase in contact time caused only insignificant changes in the removal of ammonia.

Catalytic Decomposition of Nitrous Oxide

To effect a complete removal of NH_3 as N_2 , nitrous oxide (N_2O) formed during the low temperature oxidation of ammonia by active catalysts must be decomposed into its elements. For this purpose, selected catalysts

TABLE 1. LOW TEMPERATURE CATALYTIC OXIDATION OF AMMONIA

(Nominal composition of feed gas: 1000 ppm NH₃, 10.5% O₂, 89.4% N₂)

Catalyst*	Active** Ingredient	Test Temp., °C	Feed NH ₃ , ppm	NH ₃ , ppm	Product N ₂ O, ppm	NO _x , ppm	NH ₃ Removal, %	Selectivity for N ₂ O, %
1. Catalysts of Low Activity								
HW-0101	WO ₃	250	1050	887	ND	ND	15	0
		300	928	775	ND	ND	20	0
HZn-0701	ZnO	250	1084	1034	ND	ND	9	
		300	718	589	15	ND	18	24
HMo-1201	MoO ₃	200	1091	1091	ND	ND	0	0
		250	760	717	23	ND	6	100
		300	861	818	15	ND	6	70
HV-0601	V ₂ O ₃	250	928	928			0	0
		300	908	685	ND	ND	28	0
G-61	CoO on Kieselguhr	250	1143	173	210	9	84	43
		300	979	153	250	12	85	61
HZn-0602	ZnO-Cr ₂ O ₃	200	908	520	ND	ND	43	0
		250	633	123	170	ND	81	67
		300	918	41	245	ND	95	56
MS-26599	MnO-CuO	200	1071	20	190	ND	98	36
		250	959	10	160	ND	99	34
		300	928	10	265	ND	99	57

TABLE 1. LOW TEMPERATURE CATALYTIC OXIDATION OF AMMONIA (Con't.)

(Nominal composition of feed gas: 1000 ppm NH_3 , 10.5% O_2 , 89.4% N_2)

Catalyst*	Active** Ingredient	Test Temp., °C	Feed NH ₃ , ppm	Product		NO _x , ppm	NH ₃ Removal, %	Selectivity for N ₂ O, %
				NH ₃ , ppm	N ₂ O, ppm			
Ru-05	Ru	200	724	194	98	ND	74	37
		250	908	82	195	ND	91	47
		300	826	20	205	ND	97	51
G-51	CoO-MoO ₃	200	734	551	ND	ND	23	0
		250	1652	1173	ND	ND	27	0
		300	1275	979	ND	ND	24	0
GT-826	CoO-MoO ₃ -NiO	300	1122	1000	63	0	11	100
HFe-0301	Fe ₂ O ₃	200	1188	1050	ND	ND	9	0
		250	1010	907	ND	ND	10	0
		300	908	480	38	ND	48	18
HAg-0101	Ag	200	1081	1100	ND	ND	0	0
		250	887	745	4	ND	22	6
		300	949	399	245	ND	57	89
2. Active Catalysts								
HNi-0302	NiO	200	1040	805	ND	ND	24+	0
		250	877	<10	315	ND	100	72
		300	836	<10	315	9	100	75

TABLE 1. LOW TEMPERATURE CATALYTIC OXIDATION OF AMMONIA (Con't.)
(Nominal composition of feed gas: 1000 ppm NH₃, 10.5% O₂, 89.4% N₂)

Catalyst*	Active** Ingredient	Test Temp., °C	Feed NH ₃ , ppm	NH ₃ , ppm	Product N ₂ O, ppm	NO _x , ppm	NH ₃ Removal, %	Selectivity for N ₂ O, %
Rh-05	Rh	200	1061	877	ND	ND	17	0
		250	855	214	120	ND	75	37
		300	836	<10	190	12	100	45
HMn-0201	MnO ₂	200	1194	551	150	ND	54	47
		250	928	10	460	ND	99	100
		300	954	<10	425	3	100	89
GT-302	CoO	200	1193	612	ND	ND	48	0
		250	928	82	350	3	91	83
		300	724	<10	340	ND	100	94
Pt-05	Pt	200	724	<10	230	ND	100	64
		250	958	<10	320	ND	100	67
		300	908	<10	300	ND	100	66
GT-309	Pt Oxide	200	1367	592	15	ND	55	4
		250	908	41	350	ND	95	81
		300	967	<10	440	ND	100	91
HPd-0505	Pd	200	1163	734	ND	ND	36	0
		250	1175	40	130	ND	100	22
		300	949	<10	230	ND	100	48

TABLE 1. LOW TEMPERATURE CATALYTIC OXIDATION OF AMMONIA (Con't.)
(Nominal composition of feed gas: 1000 ppm NH_3 , 10.5% O_2 , 89.4% N_2)

Catalyst*	Active** Ingredient	Test Temp., °C	Feed NH ₃ , ppm	NH ₃ , ppm	Product N ₂ O, ppm	NO _x , ppm	NH ₃ Removal, %	Selectivity for N ₂ O, %
HMn-0501		200	785	571	ND	ND	25	6
		250	1000	<10	350	ND	100	70
		300	1020	<10	340	6	100	67
HNi-0104	Ni on Kieselguhr	200	1020	112	53	ND	88	12
		250	836	20	150	ND	98	37
		300	908	20	180	Trace	100	40
HNi-1601	NiO-CoO- Fe ₂ O ₃	200	1142	856	36	ND	27	25
		250	1724	<10	435	ND	100	71
		300	928	<10	288	15	100	62
DA-SVT	Chromia- Alumina	200	1162	173	169	ND	83	34
		250	1122	61	257	ND	94	48
		300	796	<10	362	ND	100	91
GT-1065	Promoted Pd	200	908	285	ND	ND	69	0
		250	1000	328	125	ND	68	37
		300	1020	51	250	ND	95	52
3. Catalysts Producing High NO _x Concentrations								
HCo-0108	Co on Kieselguhr	200	1142	10	265	ND	98	47
		250	1050	122	315	12	88	67
		300	979	<10	360	64	100	74

TABLE 1. LOW TEMPERATURE CATALYTIC OXIDATION OF AMMONIA (Con't.)

(Nominal composition of feed gas: 1000 ppm NH_3 , 10.5% O_2 , 89.4% N_2)

Catalyst*	Active** Ingredient	Test Temp., °C	Feed NH_3 , ppm	Product		NO_x , ppm	NH_3 Removal, %	Selectivity for N_2O , %
				NH_3 , ppm	N_2O , ppm			
HCo-0901	CoO-CuO	200	1112	<10	25	Trace	99	4
		250	1050	20	140	14	98	27
		300	1000	<10	250	76	99	50
HCu-0307	CuO	200	1122	306	140	ND	72	34
		250	1000	163	215	44	83	51
		300	694	122	205	67	96	72

ND = Not Detectable

* The first letter of the catalyst identification code indicates the supplier (i.e., H=Harshaw, G=Girdler, D=Davison, M=MSA), followed by the supplier's catalog listing. The Pt, Pd, Rh, and Ru catalysts were obtained from the Engelhard Industries, Inc., unless indicated otherwise.

** Active ingredient deposited on activated alumina, unless indicated otherwise.

were screened to determine their activities for the N_2O decomposition. Each catalyst was tested under identical conditions using a catalyst bed of 50 cc, feed gas space velocity of 1200 hr^{-1} , and temperatures of 300° , 400° , and 500°C (572° , 752° , and 932°F). Feed gas was prepared by dynamic mixing of measured streams of N_2O containing gas (5218 ppm of N_2O in nitrogen) with air in proportions to obtain a nominal 1000 ppm concentration of N_2O .

The results of tests with 27 catalysts are summarized in Table 2. The activity of each catalyst is indicated by the percent of N_2O removed, calculated from the measured N_2O concentrations in feed and in product gases. The product gases were also analyzed for NO_x ; however, formation of NO_x was never observed (except in one case indicated in Table 2).

The experimental results indicate that a complete decomposition of N_2O can be achieved at temperatures of $400^\circ - 500^\circ\text{C}$. The most active catalysts are Ru, Pt, and Rh, followed by oxides of Ni and Co.

Dual-Catalyst Tests

Catalyst screening identified catalysts capable of oxidizing gaseous NH_3 to a mixture of N_2 and N_2O and catalysts suitable for the complete decomposition of N_2O . Selected NH_3 oxidation catalysts were combined with a selected N_2O decomposition catalyst into a dual-catalyst arrangement and tested for obtaining the over-all conversion of NH_3 into N_2 and H_2O . Ammonia containing gas was first passed through a 50 cc bed containing an oxidation catalyst maintained at $200^\circ - 300^\circ\text{C}$ ($392^\circ -$

Table 2. CATALYTIC DECOMPOSITION OF NITROUS OXIDE

(Nominal composition of feed gas: 1000 ppm N_2O , 10.5% O_2 , 89.4% N_2)

Catalyst	Active Ingredient*	Percent N_2O removed at		
		300°C	400°C	500°C
Ru-05	Ru	79	100	100
		97	98	100
Pt-05	Pt	24	100	100**
		22	82	100
Rh-05	Rh	44	93	100
		75	100	100
HPd-0505	Pd	0	46	83
GT-1065	Promoted Pd	0	0	0
GT-309	Pt oxide	15	5	33
HAg-0101	Ag	9	13	17
GT-302	CoO	0	4.5	23
Ho-0108	Co on Kieselguhr	27	70	99
G-61	CoO on Kieselguhr	10	55	95
HNi-0302	NiO	0	5	76
HNi-0104	Ni on Kieselguhr	30	74	100
		0	50	98
HCu-0307	CuO	0	29	46
HMn-0201	MnO_2	24	18	29
HMn-0501	MnO_2	0	0	0
HV-0601	V_2O_3	-	0	0
HZn-0701	ZnO	0	0	0
HZn-0602	$ZnO-Cr_2O_3$	0	0	0

Table 2. CATALYTIC DECOMPOSITION OF NITROUS OXIDE (Con't.)

(Nominal composition of feed gas: 1000 ppm N_2O , 10.5% O_2 , 89.4% N_2)

Catalyst	Active Ingredient*	Percent N_2O removed at		
		300°C	400°C	500°C
HFe-0301	Fe_2O_3	0	14	43
HW-0101	WO_3	0	0	0
HMo-1201	MoO_3	0	0	15
HCo-0901	$\text{CoO} - \text{CuO}$	7	10	97
G-51	$\text{CoO} - \text{MoO}_3$	-	5.5	31
GT-826	$\text{CoO} - \text{MoO}_3 - \text{NiO}$	0	0	33
MS-26599	$\text{MnO} - \text{CuO}$	17***	2	77
HNi-1601	$\text{NiO} - \text{CoO} - \text{Fe}_2\text{O}_3$	34	29	95
DA-SVT	Chromia-Alumina	21***	0	31

* Active ingredient deposited on activated alumina, unless indicated otherwise.

** At 500°C, product contains traces of NO_x .

*** Adsorption on catalyst.

572°F); the resultant product was then passed directly through another 50 cc bed containing a decomposition catalyst at 350°-500°C (662°-932°F). The final product was analyzed for NH_3 , N_2O , and NO_x .

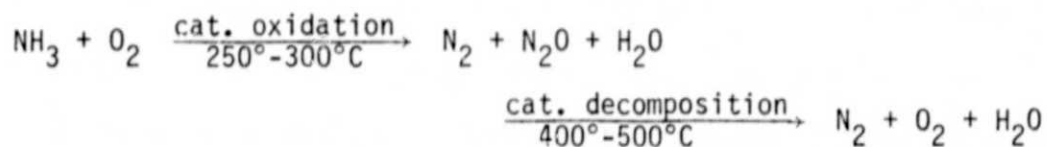
Table 3 summarizes the results of the dual-catalyst experiments. Five different catalysts were used for the oxidation of ammonia in conjunction with Ru-05 as the N_2O decomposition catalyst. A complete decomposition of N_2O was obtained only when the decomposition catalyst was maintained at 400°C (752°F); when the temperature was decreased to 350°C (662°F), N_2O was detected in the effluent. In systems #1 and #2, where nickel containing catalysts were used in the oxidation bed, the effluent gas contained some NO_x .

Table 3. AMMONIA REMOVAL BY DUAL-CATALYST ARRANGEMENT
(Feed Gas: 1000 ppm NH_3 , 10.5% O_2 , 89.4% N_2)

System #	NH_3 Oxidation Bed		N_2O Decomposition Bed		Effluent Gas, ppm		
	Catalyst	Temp., °C	Catalyst	Temp., °C	NH_3	N_2O	NO_x
1	HNi-1601	250	Ru-05	400	ND	ND	10
2	HNi-0302	300	Ru-05	400	ND	15	4
		250		400	ND	ND	14
3	Ru-05	300	Ru-05	400	ND	ND	ND
		250		400	ND	ND	ND
		250		350	ND	15	ND
4	Pt-05	250	Ru-05	400	ND	ND	ND
		200		400	ND	ND	ND
		200		350	ND	59	ND
5	Pd-05	300	Ru-05	400	ND	ND	ND
		250		400	ND	ND	ND

ND = Not Detectable

The results obtained with the dual-catalyst arrangement demonstrate the feasibility of a complete removal of NH_3 from gas mixtures according to the following scheme:



When suitable combination of catalysts is employed, the formation of the undesirable NO_x is avoided, and the final products are N_2 , O_2 , and water vapor. However, it is important to achieve a complete oxidation of NH_3 into N_2 and N_2O by the oxidation catalyst because the unreacted NH_3 reaching the decomposition catalyst bed is oxidized at higher temperatures that cause the production of undesirable NO_x .

REMOVAL OF AMMONIA FROM URINE VAPOR

Selected dual-catalyst bed combinations found to be the most effective for the removal of NH_3 in tests with artificial gas mixtures were evaluated with actual urine vapor. Tests were performed in an experimental arrangement presented schematically in Figure 2.

Untreated urine was evaporated in a 5-liter Pyrex glass flask heated by an electric heating mantle. The rate of evaporation was controlled by the power input to the heating mantle. Air was added to the urine vapor in proportions required to obtain approximately 10% oxygen in the mixture. Efforts were made to approximate the total flow rates through the catalyst beds employed in screening tests with artificial NH_3 - air mixtures, i.e., space velocity of 1200 hr^{-1} .

The urine vapor-air mixture was passed through a 30 mm ID Pyrex glass reactor normally containing a 10 cm (4") long bed of a selected ammonia oxidation catalyst (catalyst volume 50 cc) maintained at a desired temperature in the $200^\circ\text{--}300^\circ\text{C}$ ($392^\circ\text{--}572^\circ\text{F}$) range. Initially a second catalyst bed consisting of a 50 cc bed of the N_2O decomposition catalyst was stacked on top of the NH_3 oxidation catalyst. Thus, the urine vapor exiting the oxidation catalyst was immediately passed through the N_2O decomposition catalyst. However, it was discovered that this arrangement achieved only partial decomposition of the N_2O formed in the oxidation bed. Apparently, large excess of water vapor inhibited the catalytic decomposition of N_2O . Thus, the experimental arrangement

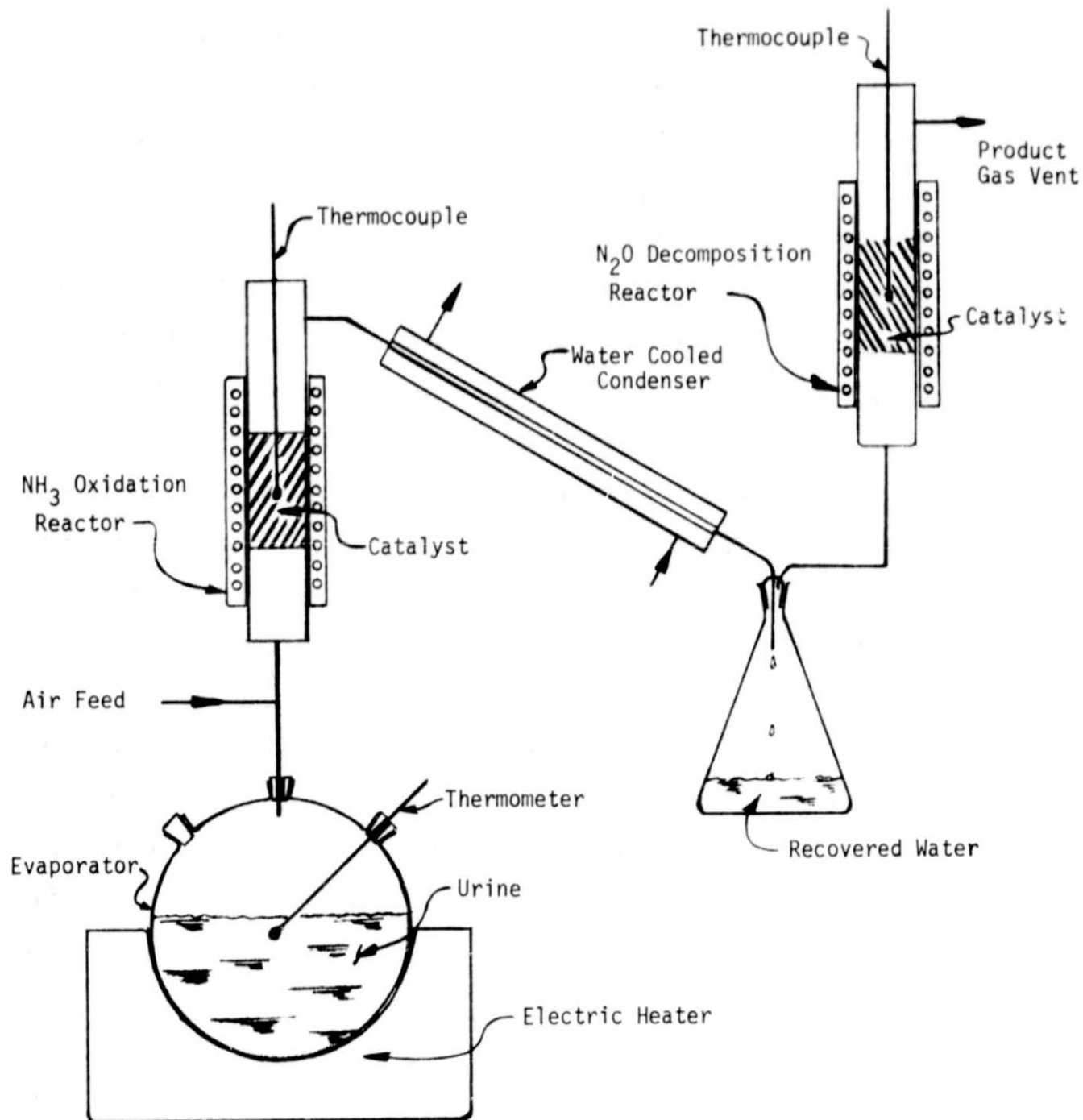


Figure 2. DUAL-CATALYST SYSTEM FOR TREATING URINE VAPOR

was changed to that shown in Figure 2 and the water vapor was condensed by a water cooled condenser situated between the NH_3 oxidation and the N_2O decomposition catalysts. The gas, freed from most of its water vapor, then passed through the N_2O decomposition catalyst maintained at $400^\circ\text{--}500^\circ\text{C}$ ($752^\circ\text{--}932^\circ\text{F}$), and vented.

The results of these tests are summarized in Table 4. Several NH_3 oxidation catalysts were investigated; however, the Pt-05 catalyst was used for N_2O decomposition in all the tests. The final effluent gas was routinely analyzed for N_2O , NO_x , and NH_3 by methods described previously. The quality of the recovered water was checked by measuring its pH and determining the NH_3 (present as NH_4^+) concentration for each test and analyzing some samples for other parameters indicated in Table 4. Testing methods described in "Standard Methods for the Examination of Water and Wastewater", 13th Edition were used.

The sterility of selected samples of the recovered water was tested by the dilution tube method both for coliform and for total viable organisms. Coliforms were not observed in any sample. Viable organisms were absent in recovered water obtained with the NH_3 oxidation bed maintained at temperatures above 200°C ; however, a sample of water recovered with the oxidation catalyst maintained at 190°C contained 2.2/ml of total viable organisms.

Although the evaporation rate of urine was constant, the concentration of NH_3 in feed varied from approximately 1,500 ppm to 4,000 ppm and was impossible to maintain constant. This may have had some influence

Table 4. REMOVAL OF AMMONIA FROM URINE VAPOR

Cat. Bed #1 NH ₃ Oxidation		Cat. Bed #2 N ₂ O Decomposition		Urine Distil. Rate, cc/min	Air Feed, cc/min	Product Gas N ₂ O, ppm		Condensed Water							
Catalyst	Temp., °C	Catalyst	Temp., °C			After Cat. Bed #1	Final Effluent	pH	NH ₃ , mg/l	TOC, mg/l	Nitrate N, mg/l	Nitrite N, mg/l	Turbidity, JTU	Conduct., μmhos	Solids, mg/l
Pt-05	300	Pt-05	500	20	500		ND	3.5	1.0	3					
	260		500	28	200		ND	3.6	ND	2	0.8	0.6			
	240		400		500		104	3.6	ND	2	1.7				
	190		500	25	500		ND	4.5	ND	4	0.5	0.6			
	200		500	35	500	326	ND	6.0	2.0	4	0.3	0.3	0.2	16	ND
HPd-0505	250	Pt-05	500	30	500	ND	ND	9.5	2700						
	300		500	30	500	189	ND	3.4	2.1	1					
DA-SVT	200	Pt-05	500	35	500		ND	4.8	0.6						
	250		500	35	500	25	ND	3.6	0.5	1	0.8	0.2	0.02	26	ND
	300		500	35	500	53	ND	6.3	0.8				0.1	52	ND
MS-26599	200	Pt-05	500	40	500	85	ND	5.1	ND	ND	0.6	0.2			
	250		500	40	500	162	ND	6.0	2.6	2					
	300		500	40	500	1217	ND	3.2	5.0	4	17.5	7.5			
HNI-1601	250	Pt-05	500	10	500	37	ND	9.5	1560						
	300		500	10	500	47	ND	9.4	2600						
	300		500	10	2000	72	ND	9.0	111						
HV-0601	600	Pt-05	500		500	120	ND	2.2	10.6						

ND = Not Detected

on the quality of the reclaimed water because the size of the catalyst bed may have been too small for handling the higher concentrations. The concentration of the total organic carbon (TOC) in feed varied also, but generally was in the 900 ppm range.

Test results indicate the feasibility of ammonia removal from urine vapor by a dual-catalyst arrangement. With suitable NH_3 oxidation and N_2O decomposition catalysts, the final gas effluent, from which water has been removed, contains no NH_3 , N_2O , or NO_x . Typical parameters of water reclaimed from urine vapor are presented in Table 5. The quality of the recovered water is acceptable, with the exception of a generally low pH. The low value of pH cannot be explained by the presence of low concentrations of nitrates and nitrites. However, urine vapor contains various sulfur containing organic compounds whose oxidation may produce acidic products that contribute to the decrease of pH of the recovered water.

Table 5. TYPICAL QUALITY OF RECOVERED WATER

Parameter	Measured Value
pH	2.7 - 4.4
Color	None (clear)
Turbidity	0.02 - 0.1 JTU
Resistivity	~0.05 megohms/cm
NH_3	0 - 1.0 mg/l
Nitrate & nitrite N	0.6 - 1.8 mg/l
TOC	0 - 5 mg/l

In addition to the removal of NH_3 , the dual-catalyst bed treatment of urine vapor also removes organic carbon and can achieve an adequate sterilization of the reclaimed water.

CONCLUSIONS AND RECOMMENDATIONS

Based on test data obtained during this investigation, the following conclusions can be made:

1. The feasibility of ammonia removal from urine vapor by a dual-catalyst system has been demonstrated.
2. Water recovered from urine vapor is of good quality, as measured by the usual parameters, but has a low pH.
3. The final gas effluent from which water vapor has been removed is innocuous and contains no undesirable components.
4. The system also removes organic carbon from urine vapor.
5. With the NH_3 oxidation catalyst operating at temperatures above 200°C (392°F), the sterilization of urine vapor is achieved.

The results of this feasibility study warrant further development of the dual-catalyst system for urine vapor treatment and recovery of potable water. Therefore, further investigation of the system is recommended for achieving the following basic objectives:

1. Additional testing aimed at selection of the best NH_3 oxidation and N_2O decomposition catalyst combination and determination of the optimum experimental conditions, particularly temperatures, air or oxygen requirements, and urine vapor flow rates.
2. Endurance tests to determine possible changes in catalyst activity and their effect on the quality of recovered water and the effluent gas; also, effects of increasing solids content in urine after

prolonged evaporation.

3. Determination of reasons for the low pH obtained and possible modifications leading to a pH in the 6 - 8 range.

4. Obtaining data for the preliminary design of a man-rated system and estimation of power, weight, and volume penalties.

BIBLIOGRAPHY

A. Oxidation of Ammonia

1. Il'chenko, N. I.; Avilova, I. M.: Kinet. Katal. 16(6), 1455-60 (1975)
2. Il'chenko, N. I.; Golodets, G. I.: J. Catal. 39(1), 57-72 (1975)
3. Il'chenko, N. I.; Golodets, G. I.: Teor. Eksp. Khim. 9(1), 36-41 (1973)
4. Il'chenko, N. I.; Golodets, G. I.: Katal. Katal. 12, 14-19 (1974)
5. Il'chenko, N. I.; Golodets, G. I.: Katal. Katal. 12, 19-25 (1974)
6. Il'chenko, N. I.; Golodets, G. I.: J. Catal. 39(1), 73-86 (1975)
7. Il'chenko, N. I.; Golodets, G. I.: React. Kinet. Catal. Lett. 1(2), 149-55 (1974)
8. Vrieland, E. G.: J. Catal. 32(3), 415-28 (1974)
9. Germain, J. E., Perez, R.: Bull. Soc. Chim. Fr. 5, 2042-7 (1972)
10. Giordano, N.; Cavaterra, E.; Martinotti, G.: Corsi. Semin. Chem. 5, 305-12 (1967)
11. Golodets, G. I.; Pyatnitskii, Yu. I.: Katal. Katal. No. 4, 25-41 (1968)
12. Kynev, S.; Klisurski, D.; Vateva, E.: Comp. Rend. Acad. Bulgare Sci. 15, 61-4 (1962)
13. Germain, J. E.,; Perez, R.: Bull. Soc. Chim. Fr. 5, 2042-7 (1972)
14. Al'kharov, T. G. et al.: Kinet. Katal. 11(1), 123-9 (1970)
15. Trifiro, F., Pasquon, I.: J. Catal. 12(4), 412-16 (1968)

BIBLIOGRAPHY (Con't.)

16. Schriber, T. J.; Parravano, G.: Chem. Eng. Sci. 22(8), 1067-78 (1967)
17. Epshtein, D. A.: Doklady. Akad. Nauk S.S.S.R. 74, 1101-4 (1950)
18. Morita Noriyoshi: J. Chem. Soc. Japan. 65, 542-8 (1944)
19. Andrussov, L.: Angew. Chem. 63, 21-7 (1951)
20. Krauss, Walther: Z. Elektrochem. 53, 320-5 (1949)
21. Holbrook, L. L.; Wise, H.: J. Catal. 27(2), 322-5 (1972)

B. Decomposition of N_2O

22. Winter, E. R. S.: J. Catal. 15, 144 (1969)
23. Winter, E. R. S.: J. Catal. 19, 32 (1970)
24. Redmond, J. P.: J. Catal. 7(3), 297 (1967)
25. Riekert, L. and Schuchmann, H. P.: Ber. Bundesges. Physik. Chemie 68(10), 986 (1964)
26. Amphlett, C. B.: Trans. Farad. Soc. 50, 273 (1950)
27. Dell, R. M., Stone, F. S., and Tiley, P. F.: Trans. Farad. Soc. 49, 201 (1953)
28. Schmid, G. and Keller, N.: Naturwissenschaften 37, 42 (1950)
29. Schulz, von I., Scheve, J. and Rienaeker, G.: Z. fuer anorg. und allg. Chemie 352, 231 (1967)
30. Clark, A.: "The Theory of Adsorption and Catalysis", Academic Press, New York, N.Y., (1970)
31. Krylov, O. V.: "Catalysis by Nonmetals", Academic Press, New York, N.Y., (1970)